

CR-134163

FINAL REPORT

AUTOMATED IODINE MONITOR SYSTEM

Contract No. NAS 9-13479

19 November 1973

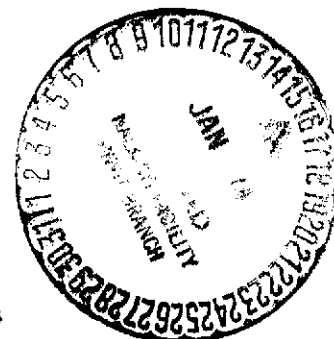
Prepared for:

National Aeronautics and Space Administration
 Lyndon B. Johnson Space Center
 Houston, Texas 77058

Beckman

INSTRUMENTS, INC.

ADVANCED TECHNOLOGY OPERATIONS
 ANAHEIM, CALIFORNIA 92806



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Introduction

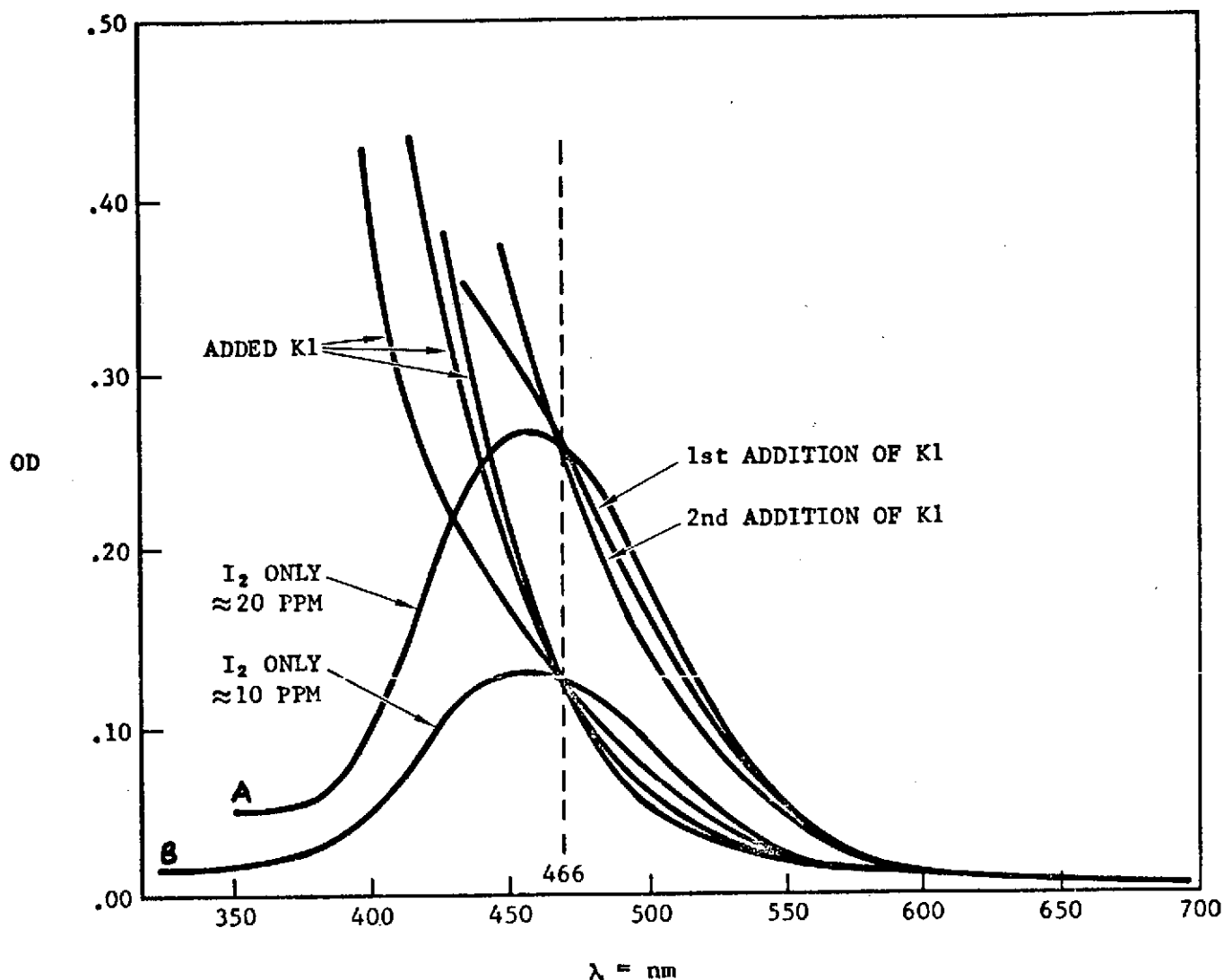
MEASURING AQUEOUS IODINE

Previous work demonstrated the feasibility of the direct spectrophotometric measurement of aqueous iodine, and the identification of the "isosbestic point" permitted iodine determination without potassium iodide interference.

Under Contract NAS 9-11879, the feasibility of a direct spectrophotometric measurement of iodine in water was established. An Iodine Colorimeter, successfully meeting the specified objectives of the project, was built to demonstrate the practicality of this technique. We next undertook further studies to verify the specificity of this method when applied to an on-line system where a reference solution cannot be used. These studies resulted in a preliminary design for an automated iodine measuring and controlling system meeting the desired specifications (NAS 9-12769). An Automated Iodine Monitor/Controller System (AIMS) based on this preliminary design has been built, tested, and delivered to the Johnson Space Center (NAS 9-13479). A summary of this project is presented in this report.

The AIMS is based upon the iodine spectroscopy illustrated in the figure. Curves A and B of the figure show the absorption characteristics of aqueous iodine in the visible spectrum. The spacecraft water supply may, however, contain potassium iodide (KI) in addition to iodine (e.g., Skylab). The two component mixture exhibits quite different absorption characteristics, as shown by the other curves in the figure. Increasing the KI concentration causes less absorption in the 466-700 nm region and more absorption in the 350-466 nm region. There is, then, a cross-over point (466 nm) where, for a given concentration of iodine, the absorption is constant. This point is identified as the "isosbestic point" and only at this wavelength can iodine be measured unaffected by varying amounts of KI.

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Measuring Aqueous Iodine at the Isosbestic Point. Curves A and B show the absorption spectrum of aqueous iodine at two different concentrations. The other curves show how this spectrum is altered with the addition of potassium iodide (KI) to the iodine solutions. Note the crossover point, at 466 nm, where the absorption is identical for a given concentration of iodine. This point is named the "isosbestic point". In a family of different equilibria (0-20 ppm I₂ in KI) one maximum rises and the other falls as the equilibrium shifts, but the intersection (isosbestic) remains constant. It is only here, at 466 nm, that iodine can be accurately measured without KI interference.

Approach

SOLVING THE REFERENCE PROBLEM

Since a colorless reference sample is not practical in an automated on-line colorimeter system, a dual detector, dual wavelength photometer concept eliminates the need for a reference cell.

In general, colorimetric measurements are made by zeroing the colorimeter against a blank (reference) solution followed by reading the light level transmitted (or absorbed) by the sample solution at the light absorbing wavelength. Photometric instruments, using separate cells for the sample and reference, make the zero (or blank) and sample measurements simultaneously (two detectors) or sequentially (one detector) and compare them.

As shown in the previous section, light absorption due to iodine is measured at 466 nm. The spectrogram also shows that there is essentially no absorption for this element in the 600-700 nm region. It is apparent, then, that for dilute aqueous iodine solutions, it is possible to obtain both the sample and reference measurements from light transmitted through a single cell. This can be done by using a rotating filter wheel to present the sample and reference light beams consecutively to a single photodetector for electronic processing or, in a static system, simultaneously by using two detectors each faced with an appropriate interference filter. For an automated, on-line system, the advantages of a single flow-through sample cell in the iodine colorimeter are evident.

Since the state-of-the-art of photodiodes is now such that multiple detector systems are feasible, we elected to use two detectors in a static system and thereby eliminate the additional weight, volume, and electronic complexity of a rotating filter wheel system. The straightforward approach and simplicity of the dual detector, dual wavelength configuration of the AIMS is sketched in Figure A. A schematic of the circuit for operating this system is given in Figure B.

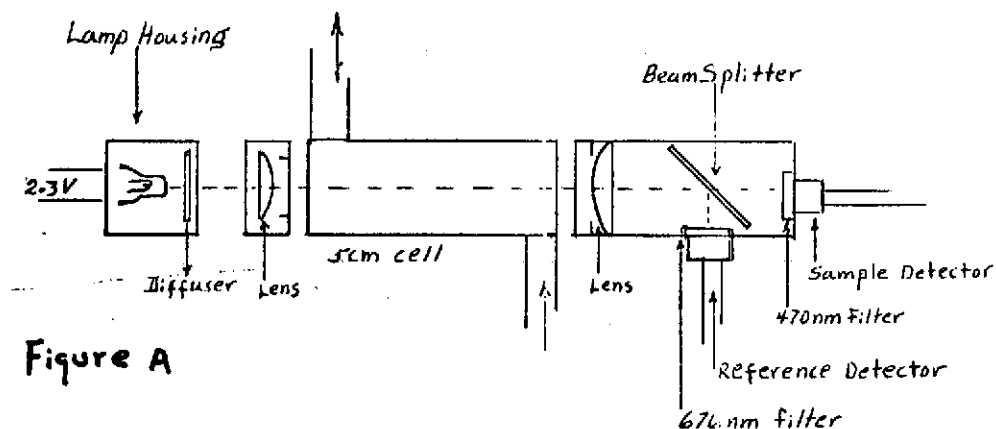


Figure A

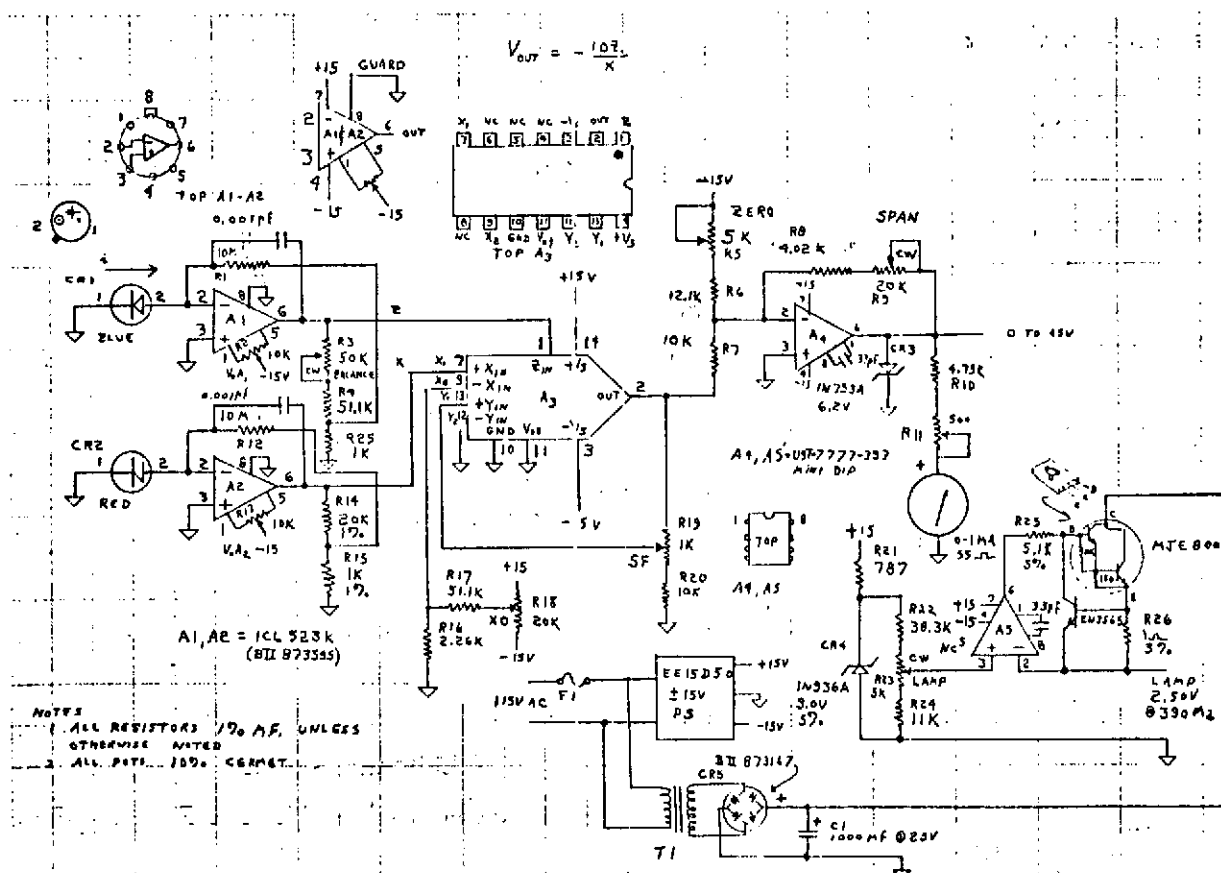


Figure B

Figure A: Sketch of Optical System of the Iodine Monitor. Using no moving parts, the system sketched here makes two light measurements at two different wavelengths through the same sample cell. A separate reference cell is thus unnecessary. Figure B shows a schematic of the electronic system used to process (ratio) the two signals from the photodiodes.

Iodine Monitor

I₂ MONITOR AND TEST SETUP DESCRIBED

An iodine colorimeter based on the concept of making two measurements simultaneously, at discrete sample and reference wavelengths, was fabricated and interfaced with a comprehensive Test Setup.

An Iodine Colorimeter based on the concept discussed in the previous section was fabricated and connected to a Test Setup as shown in the figure. Several sections in this system may be identified:

Sampling Section: The Flow-through Cell. Made of anodized aluminum, and fitted with heat absorbing glass windows, the cell is 5 cm long. Water enters and leaves at an angle, thus generating a washing action on the windows.

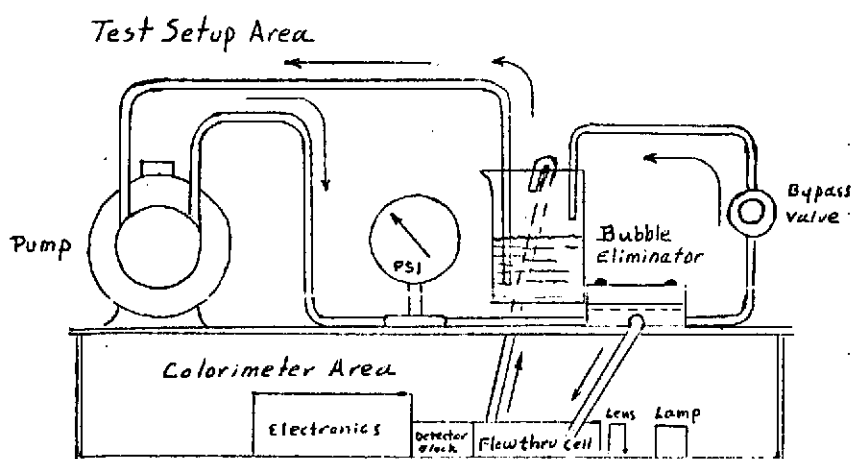
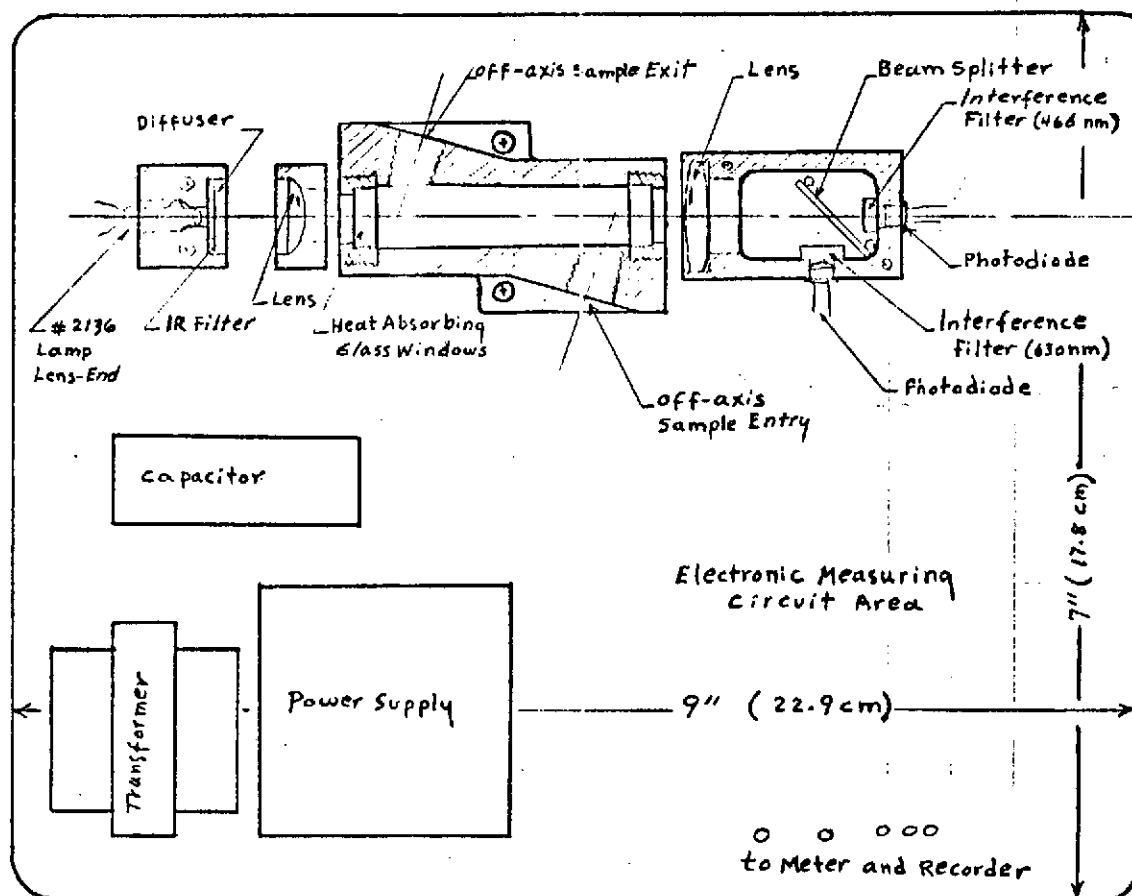
Sensor Section: Beam Splitter and Two Detectors. Collimated light from the sample cell is focused onto the detectors. A beam splitter transmits light through a 465 nm interference filter to the sample detector and reflects light through a 630 nm filter to the reference detector. The beam splitter permits each detector to "see" the same area of the sample cell window, thus any localized variation in the window clarity will not influence the output signal of one detector more than that of the other.

Power Supply and Measuring Circuit: The area occupied by the electronics is indicated. Small components are not shown.

Indicating Section: Meter and Recorder. Only the output terminals for these are shown.

Test Setup: Supply reservoir, pump, bubble eliminator, and bypass. Schematic only. The Bubble Eliminator, a simple, breadboarded device is a lucite structure which receives water pumped from the reservoir and passes part of the stream through a 0.65 μ Millipore filter to the Sample Cell. The remainder passes across the filter and returns to the reservoir. The Sample Cell outlet also returns the sampled water to the reservoir. The Bubble Eliminator filter blocks the passage of air bubbles from entering the Sample Cell (where they could disturb the accuracy and stability of the iodine measurement). The

practical requirement for the Bubble Eliminator is open to question. It can best be evaluated by testing the colorimeter in a realistic simulation of the spacecraft water supply.



Layout of Iodine Monitor and Test Setup. Only the larger electronic components are sketched. The Test Setup was used to measure accuracy, stability, and overall performance of the Monitor.

Iodine Monitor

OPTICAL ELEMENTS ANALYZED

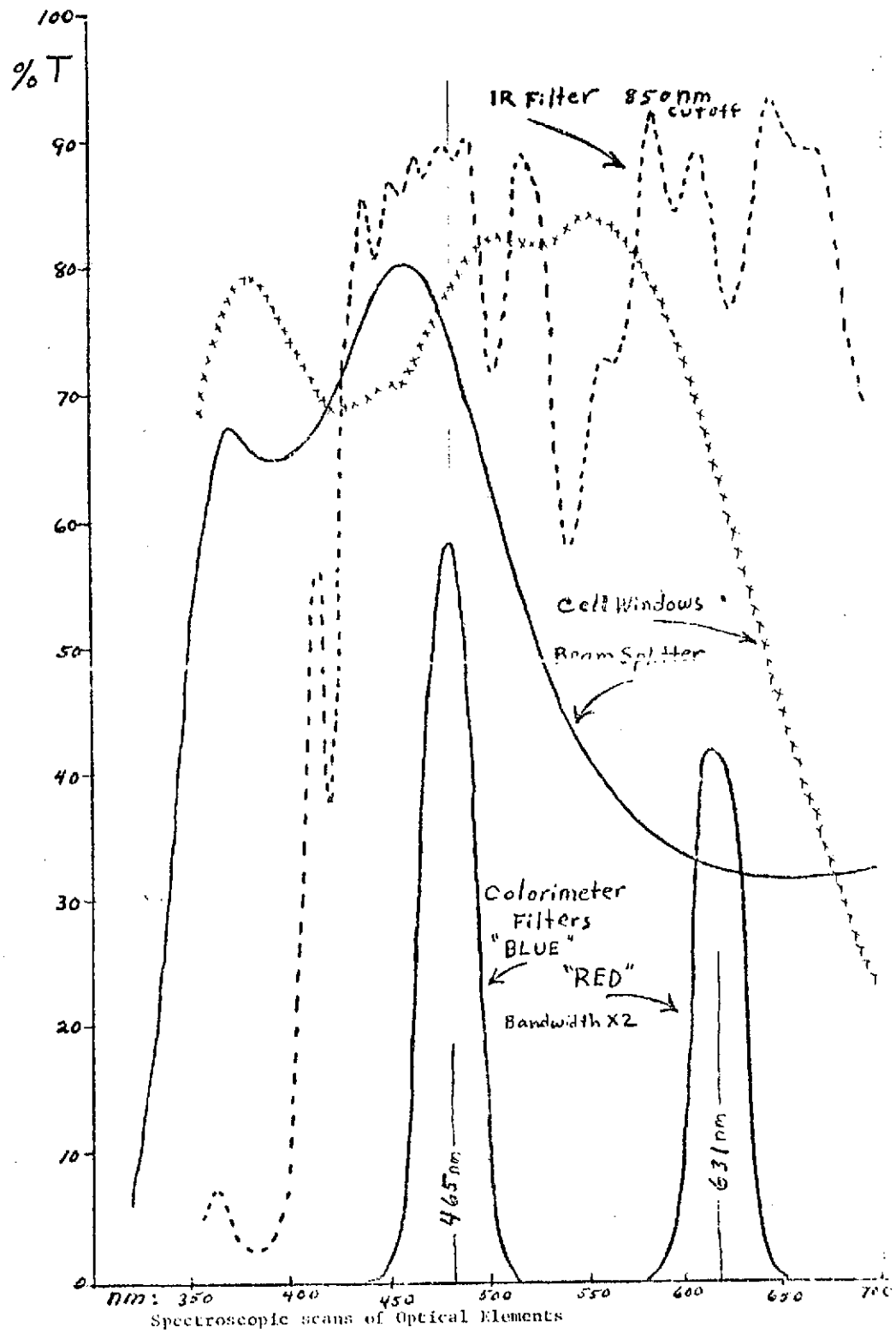
Spectroscopic scans of the optical components show that their transmittances help to equalize the sample and reference detector signals. The effect of dirty cell windows is minimal. An accessory optical element, a "Function Check Device," indicates proper instrument performance.

Spectroscopic scans of several optical elements in the Colorimeter show that the "red" signal (630 nm) is lower than the "blue" signal (466 nm). The beam splitter, IR source filter, and the heat absorbing windows in the Sample Cell also show lower transmittances in the red region of the spectrum as shown in the figure. Conversely, the spectral radiance of the tungsten lamp source and the detector response are higher in the red region than in the blue.

The net effect of absorption, radiance, and response tends to equalize the "red" and blue signals. The output of the two detectors will not, then, be as disproportionate as they would otherwise be, and thus the signal-to-noise ratio is improved.

The optical system is further enhanced by the design of the Sample Cell. The entry and exit ports are located "off-axis" and this geometry causes the sample flow to exert a washing effect across the windows to prevent deposits and help keep them clean. At the end of two month's continuous operation during which the cell windows were exposed to a variety of solutions (iodine, red ink, and dirty water), they were removed and examined. The dry windows showed a 23 percent reduction in light transmission at 466 nm. This is equivalent to the change in transmittance produced by 9 ppm I_2 . Because of the equalizing action of the two detector system the net effect, however, indicated an offset equivalent to only 0.6 ppm in iodine determinations.

An accessory optical component, a "Functional Check Device," was added to the Colorimeter. This is simply a colored filter which may be swung into the optical path, causing a meter displacement equivalent to 6 ppm I_2 --that it does so checks the stability of the span setting.



Iodine Monitor

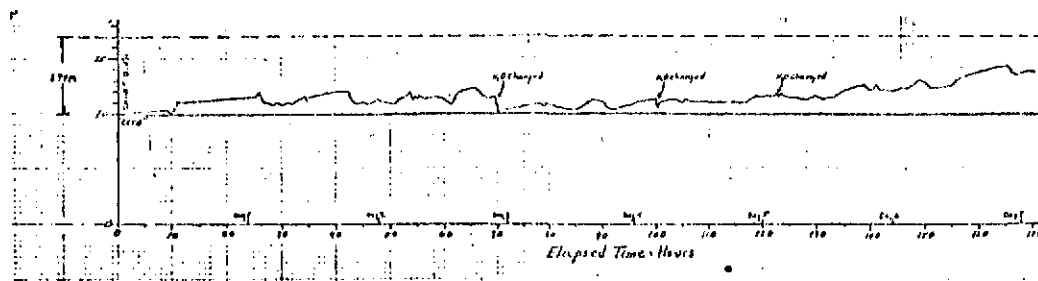
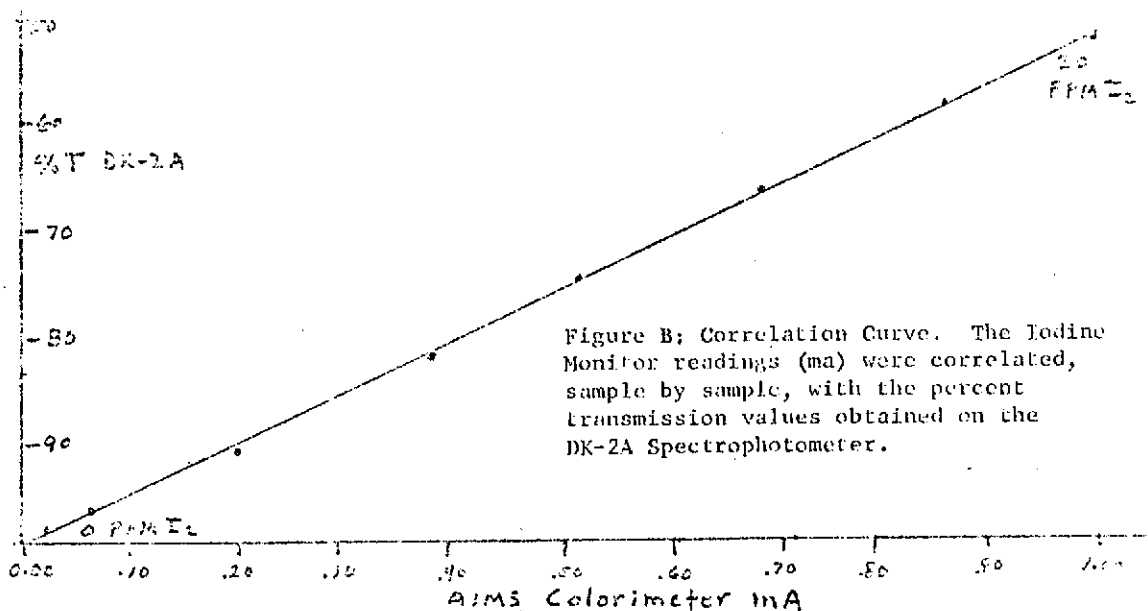
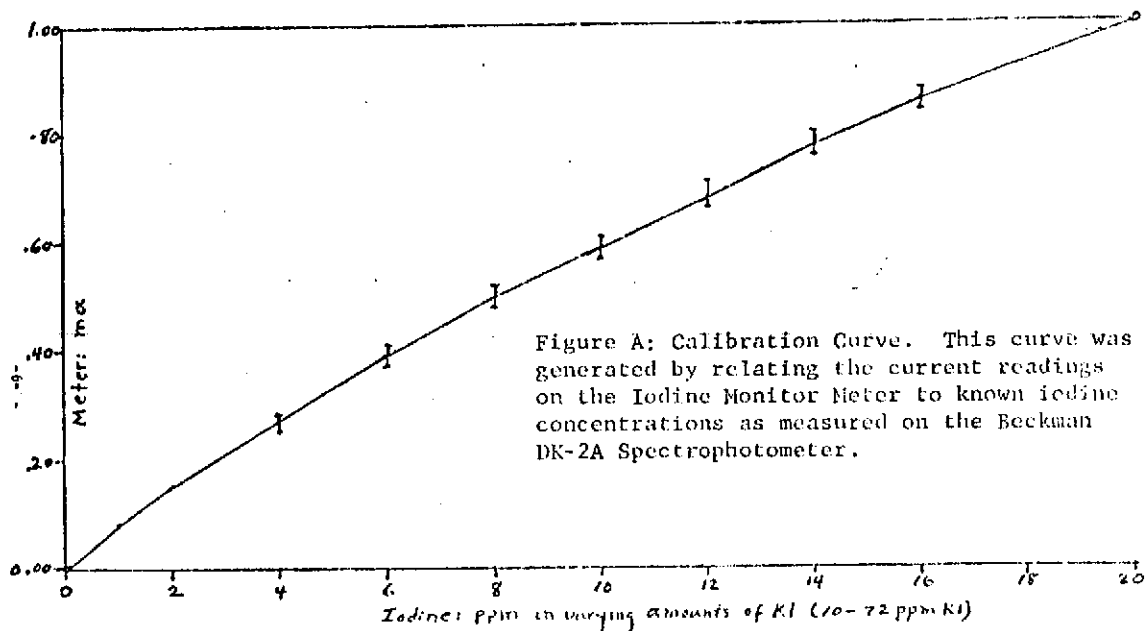
CALIBRATION AND TESTING OF MONITOR

After calibration, the Monitor showed excellent correlation with a standard spectrophotometer. A variety of tests verify that the instrument exhibits the desired performance characteristics.

Because of the evanescent nature of iodine, it is not possible to fill the sample reservoir with a solution containing a fixed amount of iodine and thus obtain an accurate meter reading. An accurate calibration of the instrument can be made, however, by adding small amounts of an iodine concentrate to the reservoir and quickly measuring the sample cell output in a standard spectrophotometer. A calibration curve of I_2 ppm versus percent transmission, previously prepared for the spectrophotometer, will then relate known iodine levels to the Colorimeter meter/recorder readings. This was done and the Colorimeter span was adjusted to make full scale on the meter correspond to 20 ppm I_2 . Figure A shows the calibration curve. The excellent correlation between the Colorimeter and the standard spectrophotometer (Beckman DK-2A) is shown in Figure B.

A stability test, lasting one week, was made. The test solution was plain water as the objective was to detect and measure any deviations from an initial zero reading with time. The water was continuously recirculated from a reservoir containing about 300 ml H_2O . The strip chart of this lengthy test is shown, greatly reduced, in Figure C. Note that the offset, equivalent to 0.3 ppm I_2 , at the end of seventy hours was returned to zero by changing the water. Two other changes, later on, did not eliminate the developed offset but, even so, the maximum departure from zero, at the end of the run, amounts to only 0.6 ppm. This offset may be caused by slow electronic drift. If so, the substitution of higher quality amplifiers (presently available) should largely eliminate this effect.

Turbidity, not exceeding ten percent, and interfering chemicals not above levels expected in a potable water supply do not significantly affect the accuracy of the iodine measurements. The instrument is not affected by being operated in various orientations.



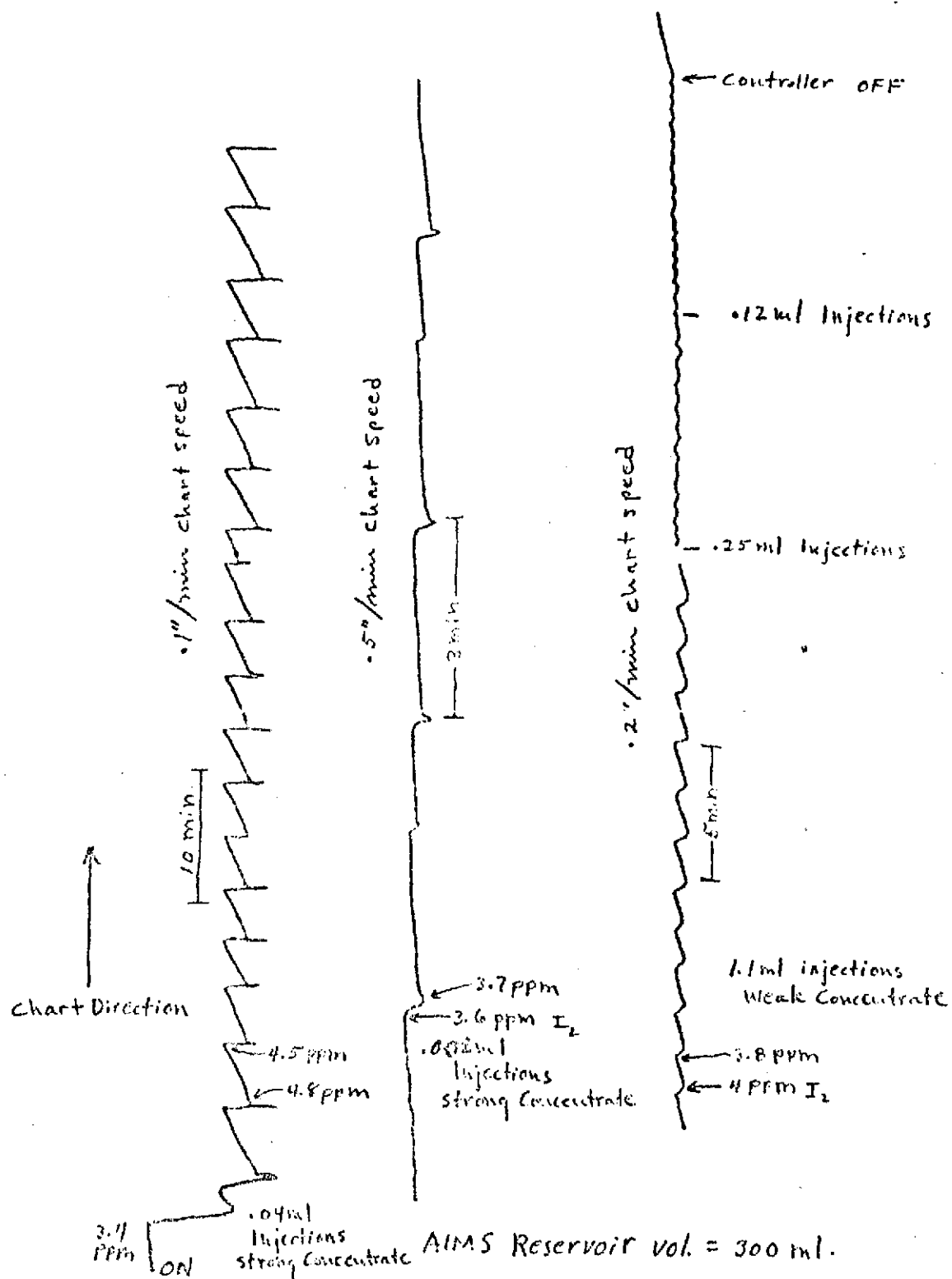
Iodine Monitor/Controller

FEASIBILITY OF IODINE ADDITION SYSTEM DEMONSTRATED

An "Iodine Addition System," conceived and breadboarded to give visibility to the feasibility of a controlled, direct injection of iodine into the water supply, has demonstrated its capability to control, within very narrow limits, the aqueous iodine level.

The breadboarded Iodine Addition System consists essentially of a single channel syringe pump operated by a special circuit which turns the pump on or off depending on the amplitude of a signal received from the Iodine Monitor. This signal may range from zero to five volts (dc) representing zero to twenty parts per million of iodine. The control circuit has a workable range of about 4.5 ppm and this span may be set anywhere in the 0-20 ppm range of the Iodine Monitor. In our instrument it was set to control from 3.5 to 8 ppm. Within this span, the plus or minus deviations around the desired level (e.g.: 4.0, 5.3, 7.2 ppm, etc.) can be maintained within very narrow limits. Examples of typical performance characteristics of the Iodine Addition System are shown in the strip chart tracings of the figure. The magnitude of the step changes shown in the runs is a function of the iodine additive concentration, the volume of water in the reservoir, the mixing time, and the volume of concentrate injected. These parameters can, then, be tailored to fit a wide range of water volumes, injection rates, and additive concentrations.

The control circuit allows the pump to be on for only 15 seconds per iodine injection. The amount injected can be regulated from 6×10^{-4} ml to a maximum of 1.6 ml. After the iodine has been added to the water supply the control circuit waits 2-1/2 minutes, then turns on to interrogate the Monitor status. If the received signal is at, or above, a preset level, the pump remains off; if the signal is below the set level, the pump is turned on for the 15 second injection event.



Recordings of Iodine Addition System. Tracings show effect of strong and weak iodine concentrates and varying injection rates.

The AIMS

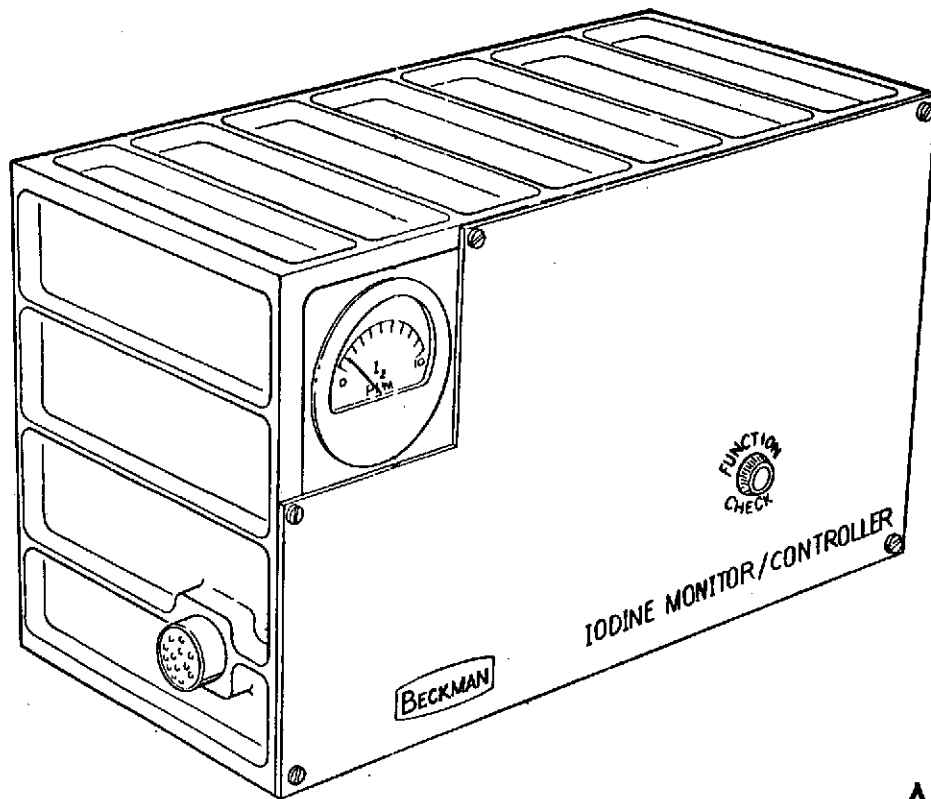
SUGGESTED FOR FUTURE WORK

Having successfully met the requirements for a prototype Automated Iodine Monitor/Controller System (AIMS), including an Iodine Addition System, the present instrumentation concept can now be modified and fabricated to comply with the special requirements of a flight type prototype system.

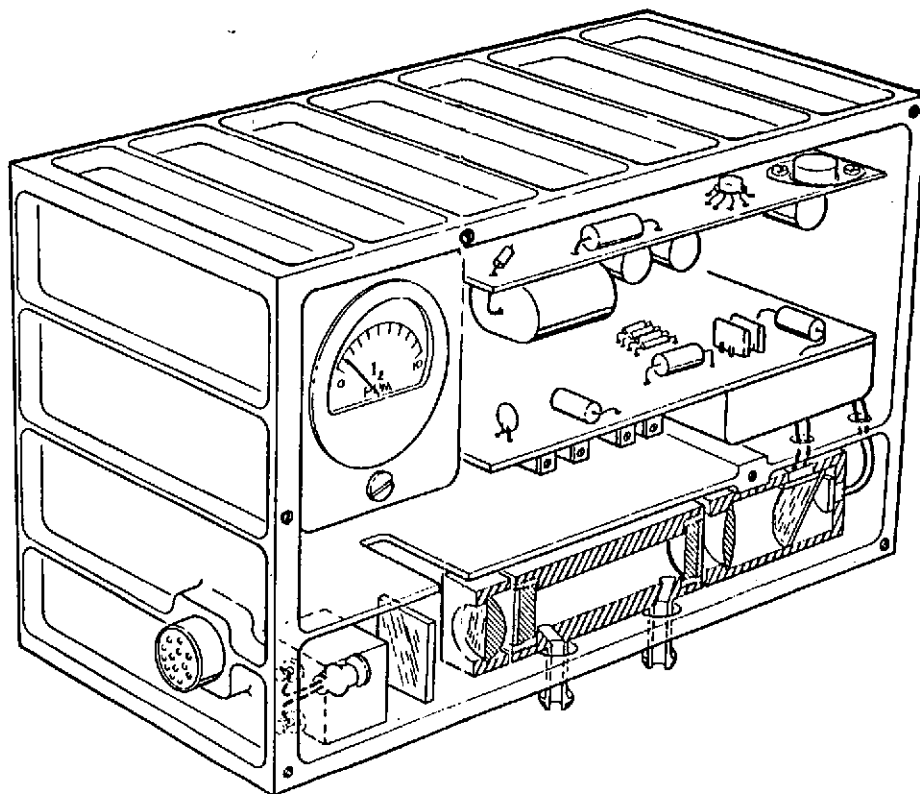
For the next phase of the Automated Iodine Monitor/Controller System project, we suggest a program comprising these tasks:

- Redesign present Colorimeter to minimize size and weight
- Fabricate system using standard parts where the form, fit and function of flight rated components will not be affected
- Design system to operate over a range of 0-10 ppm I_2 and control over a range of 2-6 ppm $I_2 \pm 1$ ppm I_2
- Design and fabricate an Iodine Addition System to interface with the Monitor
- Fabricate and test complete system.

The figure depicts our concept of the flight type Monitor package.



A



B

Concept of Proposed Iodine Monitor/Controller
(Flight Prototype Status).
A: With Cover. B: Cover Removed.